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Growth and Characterization of Zinc and Cadmium Thiogallate

by

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In an attempt to prepare infrared materials which have properties superior to those of the II-VI chalcogenides, members of the system $Zn_{1-x}Cd_xGa_2S_4$ ~~(1≥x≥0)~~ were prepared and their infrared transmission, hardness and thermal stability were measured. Whereas both $ZnGa_2S_4$ and $CdGa_2S_4$ transmitted in the infrared and have reasonable measured values for thermal stability and hardness, there is little improvement achieved by solid solutions. Keywords: Crystal growth, Infrared optical [illegible], Solid Solution, Crystal Structure, S. (rhic

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GROWTH AND CHARACTERIZATION OF ZINC AND CADMIUM THIOGALLATE

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ABSTRACT

In an attempt to prepare infrared materials which have properties superior to those of the II-VI chalcogenides, members of the system $Zn_{1-x}Cd_xGa_2S_4 (1 \geq x \geq 0)$ were prepared and their infrared transmission, hardness and thermal stability were measured. Whereas both $ZnGa_2S_4$ and $CdGa_2S_4$ transmitted in the infrared and have reasonable measured values for thermal stability and hardness, there is little improvement achieved by solid solutions.

MATERIALS INDEX: Zinc thiogallate, Cadmium thiogallate, Solid solution

Introduction

The structural and optical properties of the zinc and cadmium thiogallates have been studied by many investigators. These compounds were first synthesized by reacting the binary sulfides (1). Both crystallize with a tetragonal defect chalcopyrite structure (space group I4) (1-3). Because of the symmetry of the crystal structure, $CdGa_2S_4$ was reported to have optical activity (4). The crystals of these compounds were first grown by Nitsche et al. (5) by chemical vapor transport using iodine as the transport agent. The heat capacities (6, 7) have also been measured and solid solutions of these two compounds have been reported (8).

Little has appeared in the literature concerning the IR transmission, hardness and thermal stability of these materials. Chess et al. (9) reported the hardness of $ZnGa_2S_4$; however, the measurements were carried out on hot-pressed ceramic discs rather than on single crystals. The only report of the hardness of $CdGa_2S_4$ was made by Vengatesan et al. (10) who reported that the hardness of $CdGa_2S_4$ increased non-linearly with load. It was the purpose of this study to investigate the properties of the system $Zn_{1-x}Cd_xGa_2S_4 (1 \geq x \geq 0)$ for potential application as IR window materials.

Experimental

Sample Preparation

Single crystals of $Zn_{1-x}Cd_xGa_2S_4$, where x = 0, 0.8 and 1, have been grown by chemical vapor transport using iodine as the transport agent. The zinc metal (Gallard and Schlesinger 99.9995%) was prereduced in a Ar/H_2 (85/15) atmosphere at 200°C for 3 hours. Cadmium (Cominco American 99.9999%) was used as received. Sulfur (Gallard and Schlesinger 99.999%) was sublimed prior to use. Gallium (JMC 99.999%) was washed with warm 1M HNO_3 to remove any oxide on the surface.

For crystal growth, stoichiometric weights of elements were introduced into silica tubes which were then evacuated to 10^{-5} torr, and 5 mg/cc of iodine were added. The tubes were sealed off and enclosed in a tightly wound Kanthal coil (to even out temperature gradients) and the whole assembly was placed in a three-zone furnace. The crystal growth temperature program consisted of setting the furnace to back transport mode for one day (growth zone at 1000°C and charge zone at 800°C), equilibrating the furnace to the maximum reaction temperature for three hours, and finally, cooling the central zone at 1°C/hr to the growth temperature. For $CdGa_2S_4$, optimum crystal growth occurred when the charge zone was maintained at 880°C and the growth zone at 840°C. For both $ZnGa_2S_4$ and $Zn_{0.2}Cd_{0.8}Ga_2S$, the growth was carried out with the charge zone temperature of 950°C and the growth zone temperature of 910°C. The transport process was carried out for ten days.

Characterization

X-ray powder diffraction patterns of ground single crystals were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation (λ = 1.5405Å). For qualitative phase identification, patterns were taken with a scan rate of 1° 2θ/min, while cell parameters were determined from scans taken at 0.25° 2θ/min. Diffraction patterns were obtained over the range $12° < 2\theta < 80°$. Precise lattice parameters were obtained from these reflections using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

Optical measurements on polished single-crystal slices were performed at room temperature on a Perkin-Elmer 580 single-beam scanning infrared spectrophotometer. The measurements were performed in the transmission mode over the range 2.5 μm - 25 μm. Transmission through the sample was normalized to the signal obtained in the absence of sample.

The microhardness measurements (Knoop indenter) were made on crystals using a Kentron microhardness tester. The results were obtained using a diamond indenter with 25 gram loads.

The stability of these compounds toward oxidation was determined by heating them in a flowing oxygen stream (60cc/min) and monitoring the change in weight during the heating period. The decomposition temperature was determined as the temperature where the weight of the sample began to change. The results are summarized in Table 1.

TABLE I

Characterization of the System $Zn_{1-x}Cd_xGa_2S_4$

Sample x=	Phase Determination by X-ray	Cell Parameters a	c	IR Transmission Range (μ m)	Knoop Hardness	Decomposition Temperature (°C)
0	Tetragonal	5.296(2)	10.368(3)	2.5 - 12	367(46)	520
0.8	Tetragonal	5.488(2)	10.235(3)	2.5 - 12.5	300(16)	490
1.0	Tetragonal	5.551(2)	10.162(3)	2.5 - 13	305(15)	490

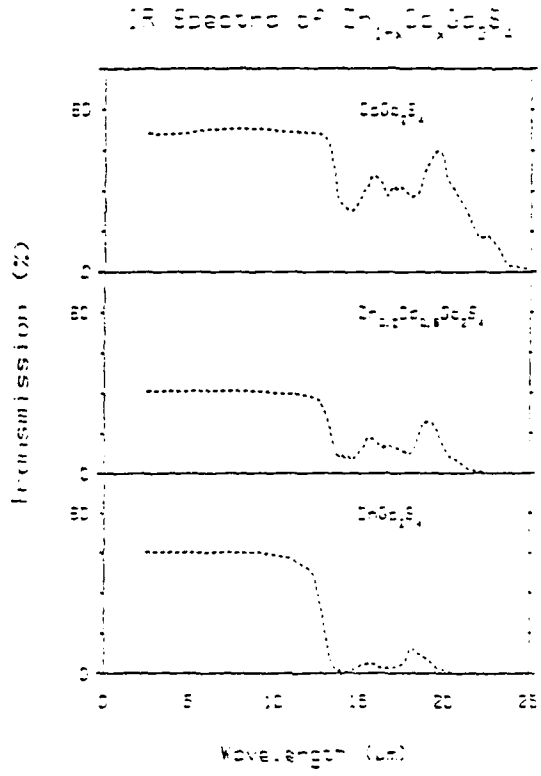

Fig. 1. Infrared spectra of cadmium and zinc thiogallate compared with that of an intermediate solid solution.

Results and Discussion

Single crystals of $Zn_{1-x}Cd_{-x}Ga_2S_4$ where x = 0, 0.8 and 1 have been grown by chemical vapor transport using iodine as the transport agent. Crystals of both $CdGa_2S_4$ and $Zn_{0.2}Cd_{0.8}Ga_2S_4$ averaged 5 x 2 x 2 mm in size and were light yellow in color. $ZnGa_2S_4$ had a strong tendency to form nuclei and its crystals had a pyramid shape with edges of about 1 mm. These crystals were colorless.

The crystalline structures of these compounds were determined by X-ray powder diffraction analysis. All three of them crystallized with a tetragonal structure. The cell parameters were determined and are given in Table I.

The IR transmission data summarized in Table I are plotted in Fig. 1. The absorption band, at about 13 μm of $CdGa_2S_4$, shifted to a shorter wavelength when zinc was substituted for cadmium. However, good transmission was obtained for all of these compounds in the range of 2.5 μm to 12 μm.

Thermal stability of these compounds towards oxidation was determined by thermogravimetric analysis. All of these three compounds start to decompose in oxygen at approximately 500°C, which is close to the stability of zinc sulfide (11). Among these three compounds, the zinc end member is slightly more stable.

Microhardness (Knoop hardness number) of these compounds is also given in Table 1. The hardness of these compounds is significantly higher than that of ZnS (11). $ZnGa_2S_4$ is slightly harder than $CdGa_2S_4$. However, substituting 20% cadmium by zinc does not improve the hardness. The measured hardness of $ZnGa_2S_4$ [367(46)] was close to Chess's result 335(30) and 454(29). Our value for $CdGa_2S_4$ is close to the value Vengatesan obtained with a 5g loading. Whereas Vengatesan reported a much higher value with a 25g load, the results in this study did not show any significant difference between a 5g or 25g load. The difference is probably due to the fact that a Knoop indenter was used in this study, whereas Vengatesan used a Vickers indenter. Because this material is brittle, a Knoop indenter would probably give more reliable results.

Conclusions

Both $ZnGa_2S_4$ and $CdGa_2S_4$ transmit in the infrared up to 12 and 13 μm respectively. However, the cadmium thiogallate decomposes at a lower temperature than the zinc thiogallate. Attempts to improve the hardness of the thiogallate by solid solution with zinc were unsuccessful. It was apparent that little improvement in the measured properties was obtained by solid solution.

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